



TITLE:

# Activation of Methyl Group by Nitro Group (V) : Some Rate Studies and Their Results

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performed for the heat treated formals and these results were shown in Table 1.

Table 1. Viscosities of heat treated formals.

Treatment	$[\eta]$	$k'$
none	0.094	0.21
200°C 5 min.	0.091	0.72
250°C 3 min.	0.077	0.77
250°C 5 min.	0.065	0.75
250°C 10 min.	0.052	0.74

in 80% HCOOH at 20°C

It was found from Table 1 that some degradation occurred at 250°C. and the  $k'$ -value in Huggins' viscosity equation slightly increased.

## 12. Activation of Methyl Group by Nitro Group. (V)

### Some Rate Studies and Their Results

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Paranitrotoluene, by acting on methanolic alkali, absorbs oxygen to give rise to *p,p'*-dinitrodibenzyl and dinitrostilbene. The authors have traced kinetically the course of oxygen absorption. Results obtained are as follows.

(1) Total oxygen absorbed is much more than the expected theoretical amount. This suggests that a certain fraction of oxygen absorbed has been employed elsewhere than in the self- condensation of *p*-nitrotoluene. Our examinations have identified several oxidation products of methanol in the reaction mixture. Theoretical amount of oxygen consumed has been calculated from the analytical data on the oxidation products as well as the yields of dinitrodibenzyl and dinitrostilbene. A little discrepancy between the observed and the theoretical in oxygen balance is probably due to the formation of a resinous matter which has been observed contaminating the main products.

Nitrobenzene or *m*-nitrotoluene does not absorb oxygen under the same experimental conditions.

(2) The absorption of oxygen proceeds according to the first order with respect to the concentration of *p*-nitrotoluene.

(3) The absorption rate does not decrease even if the air instead of oxygen is used as a reactant. This suggests, at least in a certain range, that the variation in partial pressure of oxygen little affects the rate; and so oxygen probably can not participate in the rate determining step of the reaction.

(4) The rate of oxygen absorption is markedly affected by a variation in alkali concentration. Relative mean ionic activity ( $a_r$ ) of KOH in methanol was measured electrochemically. The plots of the rate ( $dV/dt$ ) of oxygen absorption against the relative activity ( $a_r$ ) as well as its square ( $a_r^2$ ) indicate that  $dV/dt$  is proportional linearly to  $a_r^2$ , but not to  $a_r$  itself. Since the activity of undissociated alkali is given by  $a_r^2/C$ , where  $C$  is a constant, it is possible to consider that the rate of oxygen absorption increases in the first order with the activity of undissociated alkali.

(5) If the reaction held in an aqueous methanolic solution (1:7 by volume), the rate was retarded to about one third. This probably due to the decrease in activity of undissociated alkali owing to better dissociation in an aqueous methanolic solution.

### 13. Activation of Methyl Group by Nitro Group. (VI)

#### A Possible Reaction Mechanism

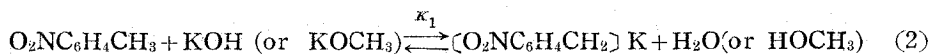
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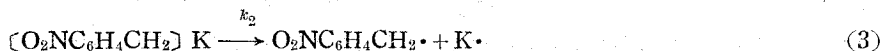
From the experimental results stated in the preceding paper, the following rate law is possible.

$$dV/dt = k_1 [p\text{-nitrotoluene}] [\text{undissociated alkali}] \quad (1)$$

where  $dV/dt$  is the rate of oxygen absorption and  $k_1$  is a rate constant. Considering the property as active methyl group in *p*-nitrotoluene, it is very reasonable to assume the following equilibrium;



where  $K_1$  is an equilibrium constant. The formation of several oxidation products of methanol suggests a radical type decomposition of the salt, i. e.,



where  $k_2$  is a rate constant.

The nitrobenzyl radicals thus formed probably combine to give rise to dinitrodibenzyl, whereas the potassium radical or atom reacts with methanol to form potassium methylate and hydrogen.



It is probably this hydrogen that absorbs oxygen, i. e., hydrogen combines with oxygen to form peroxides such as  $\text{HO}_2\cdot$  and  $\text{H}_2\text{O}_2$  which react with methanol (formaldehyde) to give rise to formaldehyde (formic acid). Thus, overall reaction is probably expressed as follows.